# Ultrafast Excited-State Dynamics and Dispersion Studies of Third-Order Optical Nonlinearities in Novel Corroles

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## Supporting Information

**ABSTRACT:** Ultrafast nonlinear optical (NLO) properties of four novel Corroles in the visible spectral range (660–800 nm) were evaluated using picosecond Z-scan technique. Ultrafast excited state dynamics have also been appraised with picosecond (ps) and femtosecond (fs) degenerate pump–probe techniques using excitation wavelengths of 800 and 600 nm, respectively. The excitation by 800 nm photons resulted in two-photon absorption at adequately high peak intensities, thereby facilitating the access to higher excited



states ( $S_n$ ). The nonradiative relaxation mechanisms from these states, reflected in the pump-probe data, consisted of doubleexponential decay with a slow component in the range of 54–277 ps and faster component in the range of 2.0 to 2.5 ps. When excited with 600 nm photons (unfocused), photoinduced absorption was observed with the first excited state  $S_1$  being populated, and as a consequence single decay was observed in the data of all molecules studied. These retrieved lifetimes were analogous to those obtained with picosecond pump-probe data. The long lifetime is attributed to nonradiative decay from the  $S_1$  state with possible contribution from triplet states, whereas the shorter lifetime is attributed to the internal conversion ( $S_2$  to  $S_1^*$ ), followed by vibrational relaxation ( $S_1^*$  to  $S_1$ ) processes. Time-resolved fluorescence lifetime measurements revealed the magnitude of radiative lifetimes to be in the nanosecond regime. NLO coefficients were evaluated from the Z-scan data at wavelengths of 660, 680, 700, 740, and 800 nm. Large two-photon absorption coefficients ( $\beta$ )/cross-sections ( $\sigma_2$ ) at 740 nm/680 nm were recorded for these molecules, making them apposite for applications such as two-photon induced photodynamic therapy and lithography. Figure of merit, *T*, was <1 for all molecules at 740 and 800 nm, suggesting that these molecules find use in photonic device applications.

## INTRODUCTION

Novel moieties with strong two-photon absorption (2PA) and three-photon absorption (3PA) cross-sections/coefficients are imperative for potential applications in the fields of photonics, lasing, photodynamic therapy (PDT), and bioimaging.<sup>1-</sup> Studies on a variety of molecules with strong 2PA/3PA have established their relevance in fluorescence spectroscopy, 3D imaging, and lithography because of high spatial resolution achieved through intensity-dependent processes.8-11 Furthermore, they encompass potential in the fields of optical data storage and optical limiting.<sup>1,4</sup> Several organic materials with large number of  $\pi$ -electrons such as porphyrins, phthalocyanines, and porphycenes possessing interesting nonlinear optical (NLO) properties and dynamics have been extensively investigated in recent times by several groups including rigorous efforts from our group.<sup>12-26</sup> Despite several studies being reported in literature, most of them failed to embark upon some of the most important issues, for instance (a) wavelength-dependent nonlinearities, (b) pulse width-dependent nonlinearities, and (c) determination of third-order nonlinearity magnitude, especially the pure electronic contribution, combined with their time response. Corroles have recently been subjected to intense research activity due to their attractive properties finding numerous applications, straddling from antitumor therapeutic properties to catalytic and important sensor applications for light energy conversion and singlet oxygen generation.<sup>27–33</sup> Corroles possess stronger fluorescence properties than their porphyrin counterparts opening up the potential for their utility in diverse areas such as cancer diagnosis. The spectral, electrochemical, and photophysical properties make these compounds promising building blocks to be used in dye-sensitized solar cells (DSSCs) with superior conversion efficiency.<sup>34,35</sup> Therefore, investigation of photophysical properties of Corroles (and similar molecules) is imperative for the potential use of these compounds.<sup>36–40</sup> Furthermore, these properties facilitate the treatment of deeper penetration into human tissue to be used as an ideal photosensitizer in PDT. Recent reports have

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suggested that Corroles are superior as PDT photosensitizers than porphyrin compounds.<sup>41</sup>

Liu et al.<sup>42</sup> demonstrated that the corroles (i) are nonplanar and encompass a larger number of Franck-Condon active vibrations, (ii) possess macrocycle framework that is rigid thereby yielding more steeply rising potential surface walls compared with metalloporphyrins, (iii) comprise S<sub>1</sub> excited states with structural displacements (relative to the ground state) that are similar to or smaller than those of their metalloporphyrin counterparts, and (iv) possess S2 surfaces that exhibit, to some extent, larger displacements (relative to the ground state) than those of the metalloporphyrins. Although the first synthesis of corroles was reported in 1965, important characterizations such as their optical nonlinearities and excited-state dynamics are being investigated only re-cently.<sup>43-49</sup> Rebane et al.<sup>43,44</sup> and Cho et al.<sup>45</sup> studied the NLO properties and reported 2PA cross-sections and spectra of corroles. Previously we had reported partial results from the NLO measurements of two novel corroles (tetraphenyl corrole (TPC) and tetratolyl corrole (TTC)).<sup>25,26</sup> The NLO coefficients extracted were promising, suggesting the potential of such molecules in the field of photonics. In this Article, we report detailed results from the ultrafast NLO and excited-state lifetime (nonradiative and radiative) measurements of four novel corroles: (a) TPC, (b) TTC, (c) germanium-substituted TTC (GeTTC), and (d) phosphorus substituted TTC (PTTC) achieved using pump-probe/time-resolved fluorescence and Z-scan techniques, respectively. A summary of performance of these molecules in comparison with others is also presented.

#### EXPERIMENTAL DETAILS

Synthesis. Both TTC and TPC were synthesized and purified as per the literature methods.<sup>28</sup> Synthesis of [P(TTC)-(OH)<sub>2</sub>]: 5,10,15-Tri-(4-methyl phenyl) corrole (100 mg, 0.19 mM) and POCl<sub>3</sub> (600  $\mu$ L, 6.45 mM) was dissolved in 20 mL of dry pyridine. The resulting reaction mixture was refluxed under a N2 atmosphere until the Q bands of Corrole had changed. Then, the solvent pyridine was removed under reduced pressure, and the obtained residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered. The filtrate was washed with dilute HCl, dried, and evaporated. The residue was subjected to silica gel column and eluted with CH<sub>2</sub>Cl<sub>2</sub>. The brown color band was collected and recrystallized from CH2Cl2/hexane to get the desired compound. Elemental analysis C37H25N4O2P (calculated mass % in parentheses): C = 75.40 (75.50), H = 4.30 (4.28), and N = 9.50 (9.52). MS(ESI) m/z 588 calculated for C<sub>37</sub>H<sub>25</sub>N<sub>4</sub>PO<sub>2</sub>. UV-visible. In CH<sub>2</sub>Cl<sub>2</sub> ( $\lambda_{max}$ ,  $\varepsilon$ , dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 647 (4.04), 616 (4.12), 575 (4.27), 415 (5.59). Synthesis of [Ge(TTC)-(OH)]: 5,10,15-Tri-(4-methyl phenyl) corrole (100 mg, 0.19 mM) and GeI<sub>4</sub> (580 mg, 1.0 mM) were dissolved in 20 mL of dry DMF. The resulting reaction mixture was refluxed under a N2 atmosphere until the Q-bands of Corrole had changed. Then, the solvent was removed under reduced pressure and the obtained residue was dissolved in CH2Cl2 and filtered. The filtrate was washed with dilute HCl, dried, and evaporated. The residue was subjected to silica gel column and eluted with CH2Cl2. The brown color band was collected and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane to get the desired compound. Elemental analysis  $C_{37}H_{25}N_4O_2P$  (calculated mass % in parentheses): C = 75.40 (75.50), H = 4.30 (4.28), and N = 9.50 (9.52). MS(ESI) m/z 588 calculated for C<sub>37</sub>H<sub>25</sub>N<sub>4</sub>PO<sub>2</sub>. UV-visible. In CH<sub>2</sub>Cl<sub>2</sub>

 $(\lambda_{\text{max}}, \varepsilon, \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$  647 (4.04), 616 (4.12), 575 (4.27), 415 (5.59).

The UV-visible spectra were recorded with a Shimadzu model 1700 spectrophotometer, and steady-state fluorescence spectra were recorded using a Spex model Fluorolog-3 spectrofluorometer using solutions with an optical density of ~0.15 at the wavelength of excitation ( $\lambda_{ex}$ ). Time-resolved fluorescence measurements have been carried out using a HORIBA Jobin Yvon spectrofluorometer. In brief, the samples were excited at 405 nm, and the emission was monitored at 605 nm in each case. The count rates employed were typically  $10^3$ to  $10^4$  s<sup>-1</sup>. Deconvolution of the data was carried out by the method of iterative reconvolution of the instrument response function and the assumed decay function using DAS-6 software. The goodness of the fit of the experimental data to the assumed decay function was judged by the standard statistical tests (i.e., random distribution of weighted residuals, the autocorrelation function, and the values of reduced  $\chi^2$ ).

The degenerate picosecond pump probe experiments<sup>23</sup> were performed using an amplified Ti:sappire laser system delivering 800 nm (central wavelength) pulses at a repetition rate of 1 kHz. The amplifier was seeded with ~15 fs pulses (80 MHz, 800 nm central wavelength, typical bandwidth of ~55 nm fwhm) from an oscillator. The pump-to-probe energy ratio was typically maintained at 10:1. The angle between pump and probe was 75 mrad ( $\sim 4^{\circ}$ ). Both the pump and probe were focused to the sample in the 5 mm quartz cuvette using a 20 cm lens. The intense pump (20  $\mu$ J/pulse, calculated after taking into account the Fresnel losses) was used to excite the molecule, whereas a low power probe beam (2  $\mu$ J/pulse) was used to monitor the transmittance of sample, ensuring that there were no self-induced nonlinearities due to the probe beam. The pulse duration was estimated to be  $\sim 2$  ps using an autocorrelation technique performed with 2 mm thick BBO crystal in the noncollinear geometry (Supporting Information). For 600 nm pump-probe experiments, we had used laser pulses at 1 kHz repetition rate obtained from an optical parametric amplifier (TOPAS-C, light conversion) pumped by a Ti:sapphire regenerative amplifier delivering ~60 fs pulses tunable in the spectral range of 260 nm to 20  $\mu$ m. Unlike in the picosecond case, unfocused pump and probe pulses were used. The pump was chopped at 100 Hz frequency. The delay for probe beam was provided through an automated translation stage that was connected to a personal computer. A lock-inamplifier determined the magnitude of signal (differential probe transmission measured with a photodiode, in units of volts) at the modulation frequency (chopper frequency). The experimental setup (Supporting Information) used for measuring the NLO properties at 800 nm in the Z-scan<sup>50</sup> configuration is discussed in detail elsewhere.<sup>21,23,25</sup>

## RESULTS AND DISCUSSION

**Picosecond NLO Properties.** The linear absorption spectra and structures of germanium tritolyl corrole (GeTTC) and phosphorus tritolyl corrole (PTTC) are shown in Figure 1. When compared with regular porphyrins, both GeTTC and PTTC also exhibited two strong bands: one in the near-ultraviolet ( $\lambda_{max} = 405 \text{ nm}$ ), the Soret band ( $\pi - \pi^*$ ), and the other in the visible spectral region (500–630 nm,  $\lambda_{max} = 590 \text{ nm}$ ). The absorption spectra were dominated by  $\pi - \pi^*$  electronic transitions with an intense and broader Soret band (B band) near 400 nm and n- $\pi^*$  electronic transitions with Q-bands higher than 500 nm. Figure 2 illustrates the emission



Figure 1. Absorption spectra of (a) GeTTC and (b) PTTC in  $CH_2Cl_2$ . Red (bottom) and black (top) solid lines are the absorption spectra recorded at low (~10<sup>-5</sup> M) and high (~10<sup>-4</sup> M) concentrations, respectively.



Figure 2. Emission spectra of (a) GeTTC (dashed), (b) PTTC (solid), (c) TTC (dotted), and (d) TPC in dichloromethane (short dashed).

spectra recorded for all molecules in dichloromethane. We noticed that PTTC molecules had the highest quantum yield. Figure 3a,b shows open and closed aperture Z-scan data of GeTTC and PTTC, respectively, obtained at 800 nm with a concentration of 1 mM. From the Figures it is evident that both molecules exhibited strong reverse saturable absorption (RSA) for higher irradiances and the magnitude of nonlinear absorption decreased for lower irradiances due to the presence of saturable absorption (SA). The switching (SA to RSA) behavior observed was probably due to saturation (followed by absorption) from  $S_1$  states (20 400-15 390 cm<sup>-1</sup>). At higher peak intensities ( $I_{00} \approx 86 \text{ GW/cm}^2$ ), the data were fitted with  $^{2}$ PA,  $^{51,52}$  and the fits obtained were good (least  $\chi^{2}$  was obtained). It is well-established that such large molecules have intricate nonlinear absorption behavior heavily dependent on the excitation wavelength, peak intensity, and concentration

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used.<sup>53,54</sup> The 2PA mentioned here refers to one photon absorption, followed by another photon absorption (1 + 1)photons). Because the pulse duration used was  $\sim 2$  ps, there is a possibility that a photon excited to S<sub>1</sub> states can relax back to the vibrational ground states of  $S_1$  before it can absorb another photon and arrive at  $S_2$  states.<sup>53,54</sup> The excitation from  $S_0$  to  $S_2$ is thus completed by the sequential absorption of two photons or in certain cases with simultaneous absorption. The presence of resonances in the spectral range of 23 100 to 27 780 cm<sup>-1</sup> (S<sub>2</sub> states) makes it possible for 2PA of 800 nm photons (12  $500 \text{ cm}^{-1}$ ) at these intensities. We had previously showed that with strong peak intensities one could even observe 3PA (involving 1 + 2 or 2 + 1 photons kind of nonlinear absorption).<sup>25</sup> The closed aperture Z-scan data demonstrated negative nonlinearity for the samples, which indicates selfdefocusing phenomena. The magnitudes of NLO coefficients were obtained by solving the propagation equations (see the Supporting Information) and fitting the experimental data. The thermal nonlinearity (due to heating) will be minimal in the case of picosecond, 1 kHz excitation. The important thing to be noted is the time ( $\sim 1$  ms) available between two successive picosecond laser pulses is sufficient to minimize any thermal effects. From the value of  $\beta/n_2$  we have calculated the magnitudes of  $\text{Im}\chi^{(3)}/\text{Re}\chi^{(3)}$ . The magnitudes of 2PA crosssections  $(\sigma_2)$  and figures of merit (T) were also evaluated (see the Supporting Information). The obtained nonlinear coefficients are summarized in Table 1. The obtained values of  $n_2$ and  $\beta$  of GeTTC/PTTC were one order of magnitude lower than those of TPC/TTC.

To establish the efficacy of these molecules in the visible spectral region (660-800 nm), we recorded Z-scan data at different wavelengths. The data for TPC and TTC at wavelengths of 680, 700, and 740 nm were reported in our previous publication.<sup>25</sup> Figure 4a,b illustrates the open aperture data (stars) and closed aperture data (open circles) of TPC and TTC, respectively, recorded at a wavelength of 660 nm and a peak intensity of 80 GW/cm<sup>2</sup>. The open aperture data clearly indicated SA, apparent from the changes in transmittance values. The concentrations of solutions used were 0.5 mM. The data were recorded for TPC and TTC at peak intensity levels, where the contribution from solvent was insignificant. Obtained experimental data were fitted using the standard equations.<sup>51,52</sup> The linear absorption for these molecules is slightly higher at 660 nm; therefore, we can expect saturation from the  $S_1$  singlet state. For lower peak intensities, population in the ground state is bleached initially ( $S_0$  states to  $S_1$  states). In general, either the excited absorption cross-section ( $\sigma_{\rm ex}$ ) is smaller than the ground state absorption cross-section ( $\sigma_0$ ) or the peak intensity is not sufficient to invoke  $\sigma_{\rm ex}$  resulting in RSA. The saturation intensities  $(I_s)$  estimated (35 GW/cm<sup>2</sup> for TPC and 52 GW/ cm<sup>2</sup> for TTC) were less than peak intensities used; therefore, we did not calculate  $\beta$ . Both the samples exhibited negative nonlinearity, as discovered by the peak-valley signature in the closed aperture data. The magnitudes of the nonlinear refractive indices  $(n_2)$  evaluated, using the standard procedure, were  $6 \times 10^{-15}$  cm<sup>2</sup>/W for the TPC and  $8 \times 10^{-15}$  cm<sup>2</sup>/W for TTC. The solvent nonlinearity was positive, suggesting that the actual values of  $n_2$  estimated for the pure solute will be higher than those calculated and presented here.

Figure 5a,b demonstrates the open aperture Z-scan data for PTTC and GeTTC, respectively, recorded at wavelengths of 660, 680, 700, and 740 nm with a concentration of 1 mM and peak intensities in the range of 90-143 GW/cm<sup>2</sup>. Unlike TPC



Figure 3. Open aperture Z-scan data of (a) GeTTC [46 GW/cm<sup>2</sup> (open circles) and 86 GW/cm<sup>2</sup> (solid circles)] and (b) PTTC [63 GW/cm<sup>2</sup> (open squares) and 83 GW/cm<sup>2</sup> (solid squares)]. (c) Closed aperture data of GeTTC (empty circles) and PTTC (solid circles) recorded with peak intensity of 70 GW/cm<sup>2</sup>. Scattered points are experimental data and solid lines are the theoretical fits. Concentration of the solutions used was ~1 mM.

Table 1. Summary of the NLO Co	efficients Estimated for All Fou	ur Corroles from the Z-scan	n Data Measured a	t Wavelengths of
800,740, 700, 680, and 660 nm				

sample	$\lambda_{ex}$ (nm)	$\binom{n_2}{(\mathrm{cm}^2/\mathrm{W})}{10^{-16}}$	$\beta$ (cm/W) $10^{-12}$	$\begin{array}{c} \text{Re} \chi^{(3)}  \\ (m^2/V^2) \\ 10^{-22} \end{array}$	$\begin{array}{c} \text{Im}[\chi^{(3)}] \ (m^2 / \\ V^2) \ 10^{-23} \end{array}$	$\chi^{(3)}$ (m <sup>2</sup> /V <sup>2</sup> ) × 10 <sup>-22</sup>	$\chi^{(3)}$ (e.s.u.) × 10 <sup>-14</sup>	$\sigma_2 (cm^4 s/photon) \times 10^{-48}$	$\delta$ (GM)	Т
GeTTC	800	-7.60	3.00	8.36	2.10	8.36	5.99	1.22	122	0.31
	740	-8.30	2.89	9.13	1.87	9.14	6.53	1.27	127	0.26
	700	-2.60	2.42	2.86	1.48	2.86	2.05	1.12	112	0.65
	680	-3.16	5.08	3.47	3.02	3.49	2.50	2.39	239	1.01
	660	-2.30	3.52	2.53	2.03	2.54	1.81	1.73	173	1.01
PTTC	800	-5.10	5.73	5.61	4.01	5.62	4.03	2.33	233	0.89
	740	-6.80	5.42	7.48	3.51	7.49	5.36	2.37	237	0.59
	700	-3.00	7.20	3.30	4.41	3.33	2.38	3.33	333	1.68
	680	-3.30	11.4	3.63	6.79	3.69	2.64	5.43	543	2.34
	660	-1.80	5.80	1.98	3.35	2.01	1.43	2.85	285	2.12
TTC	800	-60	54 ( $I_{\rm S}$ = 31 GW/cm <sup>2</sup> )	66	37.8	66.1	47.3	44.30	4430	0.72
	740	-200	$-61 (I_{\rm S} = 150 \text{ GW/cm}^2)$	220.2	39.5	220.2	157.7	54.10	5410	0.22
	700	-100	15 ( $I_{\rm S} = 8 \ {\rm GW/cm^2}$ )	110.1	9.2	110.0	78.8	14.08	1408	0.10
	680	-70	$0 (I_{\rm S} = 35  {\rm GW/cm}^2)$	77.0	0	77.0	55.2			
	660	-80	$0 (I_{\rm S} = 52 \text{ GW/cm}^2)$	88.0	0	88.0	63.0			
TPC	800	-100	28 (2PA)	110.1	19.6	110.1	78.8	23.01	2301	0.22
	740	-100	$-29 (I_{\rm S} = 200 \text{ GW/cm}^2)$	110.1	18.8	110.1	78.8	25.76	2576	0.21
	700	-80	$0 (I_{\rm S} = 28 \ {\rm GW/cm^2})$	88.0	0	88.0	63.0			
	680	-50	$0 (I_{\rm S} = 16  {\rm GW/cm^2})$	55.0	0	55.0	39.0			
	660	-60	$0 (I_{\rm S} = 35 \ {\rm GW/cm^2})$	66.0	0	66.0	47.3			

and TTC (data recorded with 0.5 mM and little lower peak intensities), both samples exhibited the RSA kind of behavior. The values of nonlinear coefficient,  $\beta$ , extracted from the fits were in the range of (2.4–11.4) × 10<sup>-12</sup> cm/W. The closed aperture data provided (see Supporting Information) the magnitude of  $n_2$  (negative) in the range of (1.8–8.3) × 10<sup>-16</sup> cm<sup>2</sup>/W. From the spectral data of NLO coefficients, we

deduced that TPC and TTC possessed similar magnitudes of NLO coefficients, but they were superior when compared with GeTTC and PTTC. When the figures of merit were calculated (taking into account the linear absorption), we again established that TTC/TPC was superior to GeTTC and PTTC. From these detailed studies, we concluded that depending on the concentration and the peak intensities used



**Figure 4.** Picosecond open aperture (open stars) and closed (open circles) aperture data of (a) TPC and (b) TTC recorded with a peak intensity  $I_{00} = 80 \text{ GW/cm}^2$  at 660 nm for a concentration of  $0.5 \times 10^{-3}$  M. Open stars and circles represent experimental data, whereas the solid lines are best fits.



Figure 5. Open aperture Z-scan data and fits at different wavelengths for (a) PTTC and (b) GeTTC. Open (black) circles are the experimental data, whereas solid (blue) lines are theoretical fits. Concentration of the solutions used was  $\sim$ 1 mM.

one could easily achieve SA/RSA in such molecules, which is extremely useful in designing photonic devices. The 2PA dispersion of corroles (TPC, TTC, GeTTC, and PTTC) in CHCl<sub>3</sub> measured over a wavelengths of 660, 680, 700, 740, and 800 nm is shown in Figure 6a–d collectively with the corresponding one-photon absorption (1PA) spectra. The lower X axis represents the transition wavelength that is common for both excitations. 1PA spectra of all molecules show a distinct and strong band in the wavelength region 400–450 nm and a progression of three or four weaker bands in the region 520–680 nm. Interestingly the NLO coefficients [ $\chi^{(3)}$  values] and the figures of merit were highest for 740 nm pumping for all samples. This enhancement in nonlinearity could be due to resonant contribution of available states in the B-band.

Femtosecond NLO Properties at 800 nm. To estimate the pure electronic nonlinearities, we performed the Z-scan studies of TTC and TPC at 800 nm using ~40 fs pulses. Open aperture scans for TPC and TTC recorded at 800 nm indicated SA behavior. The concentration of solutions used in this case was ~0.5 mM. Figure 7a,b illustrates the open aperture data (stars) and closed aperture data (open circles) obtained with an intensity of 0.9 TW/cm<sup>2</sup>. The peak intensities were calculated considering the pulse duration to be  $\sim$ 70 fs due to broadening from the optical components (neutral density filters and lenses). An independent experiment performed for measuring the pulse duration indeed confirmed the value to be 70-75 fs. The experiment was performed using Silhouette (Coherent, USA) with optical components in the path. The Z-scan data were recorded for TPC and TTC at intensity levels where the contribution from solvent is again insignificant. We found that the best fit was obtained with transmittance equation for SA. The femtosecond pulses possessed large bandwidth (~27 nm fwhm), and in combination with linear absorption at 800 nm we can only expect saturation of the S<sub>1</sub> state. For pumping with higher peak intensities, we observed supercontinuum generation from the solvent. Both samples exhibited negative nonlinearity, as discovered by the peak-valley signature in the femtosecond domain also. The magnitudes of the nonlinear refractive indices  $(n_2)$  evaluated, using the standard procedure,  $^{52}$  were 2  $\times$   $10^{-17} \rm cm^2/W$  for the TPC and 1  $\times$   $10^{-17} \rm \ cm^2/$ W for TTC. We extracted the nonlinear absorption coefficients  $(0.8 \times 10^{-13} \text{ cm/W for TPC and } 2.7 \times 10^{-13} \text{ cm/W for TTC})$ for both cases because the saturation intensity  $I_{\rm S}$  was greater than the peak intensity used. The data for GeTTC and PTTC are being recorded and will be reported elsewhere. The values of NLO coefficients estimated and presented here are within an error of  $\pm 10\%$  with contributions mainly from (a) uncertainty in spot size and thereby peak intensity measurements, (b) errors in estimation of concentration, (c) fitting errors, and so on.

The NLO coefficients of tetratolyl corrole and tetraphenyl corrole (TTC and TPC) and metallocorroles (GeTTC and PTTC) obtained from Z-scan experiments at five different wavelengths (800, 740, 700, 680, 660 nm) using picosecond pulses are summarized in Table 1. It is apparent that GeTTC had higher magnitude of  $|\chi^{(3)}|$  compared with its phosphorus counterpart at 740 and 800 nm. Moreover, the magnitude gradually decreased as we moved from 800 to 660 nm. The figure of merit, *T*, was <1 (for wavelengths up to 700 nm) for GeTTC, making them worthy candidates for photonic applications (involving nonlinear refractive index) in these wavelengths. Interestingly, the substitution of germanium and phosphorus has changed the signature of nonlinear absorption in corroles. The saturation absorption (SA) changed to a pure 2PA in the substituted cases. However, there was a sign of this



**Figure 6.** Linear (line) absorption spectra and two-photon absorption coefficients (symbols) of Corroles (a) TPC, (b) TTC, (c) PTTC, and (d) GeTTC. Bottom *X* axis presents wavelength, left *Y* axis presents absorbance (Linear Absorption), and right *Y* axis presents 2PA coefficients.



**Figure 7.** Femtosecond open aperture (open stars) and closed (open circles) of (a) TPC and (b) TTC with intensity of  $I_{00} = 0.9$  TW/cm<sup>2</sup> obtained at 800 nm for a concentration of  $0.5 \times 10^{-3}$  M. Open stars and circles represent experimental data, whereas the solid lines are best fits.

switching behavior in the case of TTC at 700 nm.<sup>25</sup> PTTC exhibited superior 2PA coefficient and therefore a higher 2PA cross-section compared with GeTTC at 800 nm. The signature of closed aperture Z-scan trace demonstrated negative nonlinearity for all the corroles. However, the solvent displayed

a positive nonlinearity (with typical  $n_2$  value of  $10^{-17}$  cm<sup>2</sup>/W). Hence, the nonlinear coefficients of these molecules are higher than those calculated and presented here. The magnitudes of NLO coefficients of metallocorroles were smaller compared with unsubstituted corroles. The nonlinearity could be enhanced further by doping these molecules in a polymer such as PMMA (poly(methyl methacrylate)). In our previous NLO studies<sup>18,20</sup> of phthalocyanines, we observed that molecular aggregation in the case of thin films has greatly enhanced the nonlinearity when compared with solutions. This approach has an added advantage that a high concentration of chromophores can be incorporated into the polymer system, thereby reducing the solvent effect and increasing the linear coefficient.

In an effort to understand the dynamics following ultrafast excitation, a series of picosecond and femtosecond pump probe experiments were performed. In the first set of degenerate pump-probe experiments, all of the molecules were excited using 800 nm, 2 ps laser pulses. Figure 8a-d depicts the excited-state dynamics of all corroles probed at a wavelength of 800 nm. At initial times after excitation, there was an ultrafast increase in the transmission of the probe beam, which indicated a ground-state bleaching (GB) followed by a recovery process. A closer look at the data reveals that the relaxation dynamics or the bleaching recovery process of these molecules consisted of two components: a fast component  $(\tau_1)$  in the early stages and a slow component  $(\tau_2)$  that governed the later part of decay. The data were fitted using a double-exponential decay function.<sup>23</sup> Figure 9 schematically explains the mechanisms involved in excitation and relaxation processes due to the 800 nm pump beam. Because the pump peak intensities used were sufficient to induce 2PA, we expect the  $S_2$  states to be populated. We propose the following mechanism for decay after excitation into the S<sub>2</sub> states. The first decay time  $(\tau_1)$  is assigned to the combination of internal conversion from S<sub>2</sub> states to highest level of  $S_1$  states (denoted by  $S_1^*$ ), followed by intramolecular vibrational relaxation in the  $S_1$  states ( $S_1^*$  to  $S_1$ 



Figure 8. Picosecond degenerate pump probe measurements at 800 nm of (a) GeTTC, (b) PTTC, (c) TTC, and (d) TPC. The jagged line (black) represents experimental data, whereas the smooth line (red) represents best fit to a double-exponential decay function. Chloroform was used as solvent. Concentration of the solutions used was  $\sim$ 1 mM.

states). For such molecules, internal conversion occurs typically in a few hundred femtoseconds and vibrational relaxation occurs within a few picoseconds. Because the pulse duration used was ~2 ps, we could not resolve those two components as we did in the case of dinaphthoporphycenes.<sup>23</sup> From S<sub>1</sub> state, population can come down to the ground state by radiative or nonradiative decay ( $\tau_2$ ). In addition to fluorescence, one also comes across such *radiationless* processes where molecules in an excited singlet state may return to the ground state without the emission of a photon, converting all excitation energy into heat (through solvent). This process is not well understood, and its efficiency is very complicated to measure. Another possible channel of nonradiative decay is the transition from S<sub>1</sub> to T<sub>1</sub> states. There are multitudes of reports<sup>55–63</sup> of multiexponential decays observed in the pump-probe dynamics in organic molecules similar to the ones investigated here. Kakade et al.<sup>58</sup> have shown that in a zinc phthalocyanine (similar molecules to ours), due to aggregation effects, a new nonradiative channel opens up with lifetimes of <100 ps recorded, whereas the radiative lifetimes observed were a few nanoseconds in magnitude. Jarota et al.<sup>59</sup> have also investigated tetrasulfonated phthalocyanines (again similar molecules to ours) and observed long lifetimes in the 150-500 ps range. They have assigned it to the  $S_1$  to  $S_0$  nonradiative decay. Howe et al.<sup>60</sup> investigated phthalocyanine and zinc phthalocyanine tetrasulfonate using pump-probe spectroscopy, and on the basis of a simple threestate kinetic model, the fast decay (10 ps) was attributed to conversion from the second to the first excited singlet state, possibly involving vibrational relaxation in S<sub>1</sub> states. They argue that there might also be a small contribution from aggregates. They mentioned that first excited-state S<sub>1</sub> subsequently decayed with a time constant of 130 ps for  $PcS_4$  and 160 ps for  $ZnPcS_4$ , respectively. This decay was due to a combination of radiative and nonradiative relaxation from  $S_1$  to  $S_0$  and intersystem crossing from S1 to the triplet state. In our case, the radiative lifetimes are too long, and we expect negligible contribution from them. We had checked for aggregation effects in our molecules because we recorded the pump-probe data at 1 mM concentration. We did observe slight changes (shift in peak positions and slight peak broadening; data are now provided in the Supporting Information) in the absorption spectra (compared with the spectra recorded at 1  $\mu$ M concentration) and, therefore, expect fractional contribution from aggregates resulting in shorter (nonradiative) lifetimes of S<sub>1</sub>. However, in the data reported by Kakade et al.,<sup>58</sup> they observed nanoaggregates with strong shifts in the absorption peaks (by 40-50 nm) compared with monomers. They used strong hydrogenbonding solvents to create the nanoaggregates. In organic solvents, though, they did not observe aggregation. Fita et al.<sup>61,62</sup> studied zinc phthalocyanines and observed 10-50 ps



Figure 9. Energy level diagram of corroles: PB is photobleaching and PIA is photoinduced absorption. Red lines represent 800 nm excitation and dark-blue lines represent 600 nm excitation. Jagged lines are for nonradiative transitions, whereas the solid lines are for radiative transitions.

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time-scale dynamics, which was attributed to the vibrational cooling (relaxation by transfer of heat to the solvent) from the  $S_1$  state. The fact that the molecule PTTC had the longest decay (of ~280 ps) among all investigated ones could be due to its unique structure with OH groups in the axial position possibly affecting the aggregation.

Kullmann et al.<sup>40</sup> studied the dynamics of a bisporphyrin and figured out four different lifetimes for monomer. The fastest lifetime (few hundreds of femtosecond) was attributed to intramolecular vibrational relaxation within the S<sub>2</sub> states, the second fastest lifetime of a few picoseconds was attributed to the decay of S<sub>2</sub>, and the slower lifetime (few tens of picoseconds) was attributed to the cooling dynamics (nonradiative) in S<sub>1</sub> states. The longest lifetime of a few nanoseconds was due to the emission decay. Liu et al.<sup>42</sup> observed S<sub>2</sub> lifetimes in the range of 0.28–2.71 ps for aluminum and gallium corroles. Similarly, fast decay times were observed in Soret-excited tetrapyrroles (MgTPP) where the internal conversion (S<sub>2</sub>–S<sub>1</sub> decay) was in few picoseconds.<sup>55</sup> Figure 10a–d shows the degenerate pump–probe



Figure 10. Femtosecond degenerate pump probe measurements at 600 nm of (a) GeTTC, (b) PTTC, (c) TTC, and (d) TPC. The jagged line (black) represents experimental data, whereas the smooth line (red) represents best fit. Chloroform was used as solvent. Concentration of the solutions used was  $\sim$ 1 mM.

data of all molecules studies obtained using femtosecond pulses at 600 nm. For 600 nm excitation, there is a clear reduction of probe transmittance at the zero delay and a slowly rising component ( $\tau_1$ ). At initial times, after excitation, there was an ultrafast decrease in transmission of the probe beam, which indicated photoinduced absorption. We fitted the data using the equation  $\Delta T/T = A \exp[-(t - t_0)/\tau]$ , where  $\Delta T$  is the time-dependent change in probe transmission induced by the pump at time 't' after the pump excitation and T is the probe transmission in the absence of pump. Our data were fitted satisfactorily using a single-exponential decay function because we used unfocused 600 nm pulses where we expect the excitation limited only to the first excited singlet state. The lifetimes estimated from the fits were ~53 ps for Ge-TTC, ~286 ps for P-TTC, ~60 ps for TTC, and ~35 ps for TPC. The fact that the triplet contribution in our case is nominal can be understood from the femtosecond data, where the excitation

is limited just to S1 states. The recovery of PIA (photoinduced absorption) after crossing over to triplets (which could typically be a few hundred picoseconds) is remote. LiLi et al.<sup>41</sup> reported intersystem crossing times of a few nanoseconds in a series of hydroxyl corroles. However, with the present data, it is difficult to rule out triplet contribution to the nonradiative decay. Further experiments with white-light probe and intensitydependent pump-probe studies will be undertaken in the near future to elucidate the various contributions. We believe that focusing the femtosecond pump and probe pulses could result in excitation into higher  $S_n$  states, thereby enabling us to resolve faster decay times (separate the internal conversion from S<sub>2</sub> to  $S_1$  states and vibrational relaxation times in  $S_1$  states), as was observed by us in the case of porphycenes whose data were recorded with similar experimental conditions.<sup>23</sup> The recovery times obtained with 600 and 800 nm excitations were similar, which confirms the nonradiative decay of S<sub>1</sub> states in both cases. The dynamics parameters are summarized in Table 2. The error in the lifetime measurements was estimated to be  $\pm 15\%$ .

 Table 2. Summary of Lifetimes Retrieved from Pump-Probe

 and Time-Resolved Emission Experiments

	picosecond data (nonradia- tive)			
sample	(ps)	$\stackrel{ au_2}{(\mathrm{ps})}$	femtosecond data (nonradiative) $\tau_2$ (ps)	radiative decay lifetime (ns)
GeTTC	2.0	54	53	1.1
PTTC	2.5	277	286	2.7
TTC	2.3	70	60	3.6
TPC	2.4	47	35	3.9

The corroles studied in this work are fluorescent molecules with quantum yields of TPC, TTC, GeTTC, and PTTC being 0.19, 0.25, 0.14, and 0.31, respectively. Figure 11a–d portrays the dynamics of time-resolved fluorescence. The radiative lifetimes (of  $S_1$  state) estimated from the fits were 1.1 ns for



**Figure 11.** Fluorescence lifetime measurements of (a) GeTTC, (b) PTTC, (c) TTC, and (d) TPC in dichloromethane solvent. The jagged line (black) represents experimental data, whereas the smooth line (red) represents best fit. Excitation wavelength was 405 nm. Concentration of the solutions used was  $\sim 1 \ \mu M$ .

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GeTTC, 2.7 ns for PTTC, 3.6 ns for TTC, and 3.9 ns for TPC. The lifetimes for PTTC and GeTTC were also measured in chloroform to check the solvent dependence. The retrieved lifetimes were similar to those observed in DCM (provided in the Supporting Information). The longer lifetimes of TPC and TTC could be one of the reasons for higher nonlinearities observed because the population can reside longer in the S<sub>1</sub> state. Liu et al.42 studied the fluorescence decay times of gallium and aluminum corroles. They observed that the S<sub>2</sub> excited states relaxed to the S<sub>1</sub> states on a subpicosecond time scale. LiLi et al.<sup>41</sup> studied the fluorescence dynamics of a series of hydroxyl corroles and recorded lifetimes in the 1-4 ns range. They also noticed that intersystem-crossing transition time of these corroles decreased sharply with the increase in the atom weight and the number of halogen atoms. Ghosh et al.<sup>27</sup> similarly examined phosphorus(V)-meso-triarylcorroles and obtained emission lifetimes in the range of 2.1 to 3.7 ns range.

Comparing the NLO coefficients of corroles with some of the recently reported molecules, Rebane et al.43,44 studied (2PA) cross-sections and spectra of corroles within a broad spectral range of excitation wavelengths, 800-1400 nm. They retrieved much lower magnitudes of cross-sections in the range of 50–130 GM, and this could be attributed to the nonresonant wavelengths used for excitation. Cho et al.45 studied the 2PA cross-sections of Corrole dimers and recorded values of 1100-4600 GM. In our case, we obtained  $\sigma^{(2)}$  values in the range of 100-5400 GM comparable to that of dimers studied by Cho et al.<sup>45</sup> Our recent studies on porphycenes indicated 2PA crosssections in the 8000-21000 GM.<sup>23</sup> However, those molecules had strong two-photon resonances when pumped with 800 nm. Belfield et al.<sup>64</sup> studied 2PA of a new fluorine derivatives using 200 fs pulses over a broad spectral range and recorded a maximum of 300 GM. Rebane et al.<sup>65</sup> investigated series of fluorenyl-based chromophores with electron-donating or electron-withdrawing substituents using femtosecond pulses and demonstrated enhancements with 2PA cross-sections in the range of 10–80 GM. Morales et al.<sup>66</sup> studied unsymmetrical fluorenyl-based chromophores, flanked on either side by electron-accepting or electron-donating groups, separated by conjugated ( $\pi$ ) moieties, and observed a cross-section of 1800 GM for one of the molecules near 300 nm wavelength. Belfield et al.<sup>67</sup> reported femtosecond 2PA cross-sections of 650 GM and 1300 GM for fluorine derivatives. Our molecules possess very good cross-sections compared with some of these molecules investigated.

Our future studies will focus on (a) extending the NLO studies with femtosecond pulses at near-IR wavelengths of 1 to 1.5  $\mu$ m, (b) attempting to dope these molecules in suitable polymer(s) and repeating the NLO studies to check for the enhancement, and (c) performing femtosecond transient absorption studies (using a white-light probe) to elucidate the complete dynamics of excited states.

## CONCLUSIONS

To summarize, the picosecond NLO properties of four novel corroles have been studied in detail and were found to be intensity-dependent. At high peak intensities two-photon absorption mechanism was observed contributing to the third-order nonlinearity. The excited-state dynamics of corroles, studied using degenerate picosecond pump—probe technique, were found to possess double-exponential decay constants with all time scales in the picosecond domain. Femtosecond pump probe data recorded at 600 nm corroborated the picosecond dynamics of  $S_1$  state. The relaxation dynamics are explained by assuming a simple three-level model consisting of  $S_0$ ,  $S_1$ , and  $S_2$ states. The observation of short-lived excited-state lifetime of  $S_1$ , in the range of 53–286 ps, is significant for applications in PDT because short-lived aggregates are expected to be inefficient in singlet-state oxygen generation. The measured fluorescence lifetimes were a few nanoseconds. It is thus of interest to study the NLO properties and excited-state dynamics of these compounds, which are likely to be the active species for PDT and exist in organic solvents such as chloroform.

#### ASSOCIATED CONTENT

## **S** Supporting Information

Schematic diagrams for picosecond and femtosecond degenerate pump-probe experiments along with details. The characterization of picosecond and femtosecond pulses obtained using autocorrelation and MIIPS technique, respectively, are also provided. Schematic for the Z-scan experiment along with closed aperture data of Ge-TTC and PTTC at various wavelengths are presented. The theoretical description for Zscan analysis has been explained in detail. The absorption spectra of all samples at lower (1  $\mu$ M) and higher (1 mM) concentrations are also included along with the emission spectra of GeTTC and PTTC in different solvents (DCM and chloroform). This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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